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Some Goods From Wool Grease

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Lanolin closely resembles the natural oils of the human skin and hair. It has an amazing capacity for holding water—it will take up twice its own weight. It has excellent emulsifying properties. Because of those qualities, it is useful as a base for medical ointments; in them, it serves as the vehicle that holds a water solution of the medicament in contact with the skin, the ideal condition for absorption by that organ. Its emollience can also be attributed to its affinity for water, because it is loss of moisture that causes skin to become hard and dry, a condition that is not benefited by greasy materials, for they tend to repel water and thus prevent its natural deposition in the tissues.

Lanolin is a purified form of the heavy mixture of fatlike waxes that protect the fleece of sheep against the weather and keep its fibers strong and supple. This mixture is only a part of the complex conglomeration of substances in the fleece. Also present is a large quantity of material called suint, which is generally considered to be the residue of dried sweat, although there is still some doubt that sheep perspire. (One classic experiment showed that there was little if any increase in the moisture content of the fleece of sheep that on a hot day were chased until they would be chased no more by men on horseback. The test confirmed that humans and horses perspire profusely under such circumstances.) Suint is water-soluble and is usually lost when water is the scouring medium, even when the wax is recovered.

Also present are varying quantities of proteinaceous material, such as weathered fiber tips, dead skin, fecal matter, and adventitious impurities, which vary according to the animal's environment—such things as sand, dirt, burs, and other vegetable matter, dip residues, paint, tar, or pitch used in branding, and moisture. A troublesome impurity is sulfur, presumably a dip residue. The term "yolk" is generally used to describe this mixture; the terms "wool grease" and "degras" usually mean the crude wax after it has been removed from the fleece and separated from the suint and heavy solids.

Three principal grades of recovered grease are on the market. The first is crude or common degras, which includes acid degras, solvent-extracted grease, and lower grades of centrifugal grease. The second is a partly refined grade known as neutral degras, neutral wool grease, or technical lanolin, and frequently further subdivided according to its free fatty acid content. Last is a highly refined, bleached, and deodorized product suitable for medicinal or cosmetic use, commonly known as lanolin (hydrous or anhydrous), but sometimes as wool fat or *adeps lanae*. "Wool wax" is the best term for this part of the yolk because it is a mixture of compounds of the class called waxes by the chemist.

The relative quantities of the components of raw (greasy) wool vary widely according to type of fleece, but the over-all average percentage composition (on a moisture-free basis) will approximate: Clean wool fiber, 50 percent; sand, dirt, burs, and other vegetable matter, 15 percent; wool wax, 15 percent; suint, 20 percent. The moisture content of raw wool varies between 6 percent and 26 percent.

All of the processes by which grease is removed from wool are primarily designed to produce a suitable fiber. The grease is a byproduct. Most wool scourers use water and a detergent for the purpose. The detergent is usually a mixture of soap and soda ash. Less frequently the water-soluble suint of the wool is used; occasionally synthetic detergents are employed. When such a method is used, the scouring liquors are discharged into the sewer.

A few scourers recover part of the grease by centrifuging, but more than half of the grease stays in the discharged liquors. Such liquors cause serious stream pollution and for many years the States in which much wool is scoured have had increasing difficulty with the problem. In Bradford, England, where about four-fifths of Britain's wool is scoured, the municipal government had to spend 14 million dollars to construct a sewage-disposal plant to cope with the pollution of the Bradford Beck and the River Aire. At one time the stagnant pool formed by the sluice gates at the juncture of the Bradford Beck and the Leeds-Liverpool Canal was described as "so corrupt that large volumes of flammable gas were given off and although it had usually been considered an impossible feat to set the River Thames on fire, it was found practicable to set the Bradford Canal on fire, as this at times formed part of the amusement of boys in the neighborhood."

Some States have prohibited disposal of wool-scouring wastes in sewers. Others undoubtedly will do so soon. When that occurs, wool processors will be required to remove essentially all of the grease from their sewage effluent. It can be done by the acid-cracking process, used in England for most of the liquors processed and by a few scourers here. The process consists in decomposing the soaps by adding sulfuric acid. That breaks the emulsion and the heavy solids can be removed by hot filtration. The melted grease and soap fatty acids separate on top of the hot water and can be separated from it by decantation. Another method, recently introduced in the United States, involves treatment of the scouring liquors with calcium hypochlorite. As in the acid-cracking process, the emulsion is broken and the grease separates. The process is said to give a satisfactory effluent, which contains little grease or putrescible substances and does not have an excessive oxygen demand.

Water scouring with soap and soda ash is the cheapest degreasing process if the scouring liquors can be run into the sewer without further treatment—but not if the grease and other material have to be removed. A possible alternative is solvent scouring. A satisfactory fiber can be produced by solvent scouring. For 50 years Arlington Mills, one of the largest wool processors, has been degreasing its wool batchwise with petroleum hydrocarbon solvents.

Solvent scouring has one definite advantage over soap scouring, an advantage that stems from the high value of the wool fiber. The fiber is agitated less during solvent scouring; hence there is less tangling, breakage, and loss of fiber during the subsequent combing and carding operations. Solvent scouring does not yield harsh or brittle fibers. The process can be so controlled that any desired concentration of grease can be left on the fiber or all can be removed and a suitable lubricant applied later. The modification of the affinity of the fibers for dyes resulting from the action of the alkali usually employed in aqueous scouring can be accomplished at will by subsequent treatment with ammonia or other suitable alkali.

Apparatus for continuous scouring with trichloroethylene has passed successfully through the pilot-plant stage, and industrial units are now being put into operation. Solvent-extraction processes recover all the grease. The water-soluble suint, which is removed from the fiber by a clear water rinse, can be recovered if desired or disposed of by sewer. In the latter case further treatment may be necessary to achieve a satisfactory sewage effluent.

Whatever methods are adopted, it is apparent that instead of our present annual production of 9 million pounds of wool grease, which is probably more than present uses normally consume (our prewar annual consumption was about 6 million pounds), perhaps as much as 150 million pounds of crude grease will be available each year. The net result will be some increase in the cost of the degreasing operation and an apparent market for only about 6 percent of the grease produced. It will therefore be necessary to increase the utilization of wool grease or face the consequences of an increased burden of cost carried by the fiber. Because of the variety and unique character of the constituents of wool grease, however, it is entirely conceivable that, with increased knowledge of their chemistry, they will return a substantial profit in their own right.

Unlike most waxes, which are hard and somewhat brittle, wool wax is soft and fatlike but tenacious to the touch. It is a mixture of esters of long-chain fatty acids with alcohols of high molecular weight. Both free acids and free alcohols are usually present. There are at least 32 different acids in wool wax. They belong to four or more different classes: Normal fatty acids, about 10 percent; the branched-chain fatty acids, with a methyl group in the penultimate position (iso acids), about 29 percent; dextrorotatory, branched-chain fatty acids, with a methyl group in the antepenultimate position (ante-iso acids), about 37 percent; optically active 2-hydroxy acids, about 4 percent; unaccounted for, about 20 percent. The ante-iso acids contain an odd number of carbon atoms; those of the other classes contain an even number.

The alcohols, which may represent roughly half the weight of the wax, belong to at least three different groups, each of which represents about one-third of the total weight of the alcohol fraction. The steroid group is represented only by cholesterol, which is the best-known constituent of wool wax. Another group, the triterpene alcohols, is represented by two compounds known as lanosterol and agnosterol. The exact structure of these compounds is not known, but they are not steroids. They differ from each other only in the number and location of double bonds. Lanosterol predominates. Apparently agnosterol is not always present. The alcohols of the third group are referred to as the wax alcohols. They include two compounds that are normal constituents of other waxes: Cetyl alcohol, a straight-chain primary alcohol containing 16 carbon atoms; and ceryl alcohol, apparently a mixture of 26-carbon alcohols. Some other alcohols have been reported as present, but their structures have not been definitely established. One is believed to be unsaturated and to contain two alcoholic (hydroxyl) groups. Still other uncharacterized alcohols belonging to this group may be present.

The crude and neutral grades of wool grease are used principally in lubricating greases, the cutting oils, leather-dressing products, carbon paper, paints, and printing inks, and for weatherproofing cordage and superfatting soaps.

Wool grease is unexcelled as a corrosion-resisting coating for metals. A concentrated solution in petroleum naphtha gives a thin but effective temporary coating, which can be easily removed when desired. For greater permanence, a resin which gives a lacquer-like coating can be added. The effectiveness of this type of coating can be increased by adding rust-inhibiting pigments, such as zinc chromate. Occasionally crude wool grease is used in bituminous emulsions for road building where the application of hot mixtures is not feasible. The Italian Government used most of the surplus grease that accumulated in the United States during the depression of the early 1930's for the construction of military roads in Abyssinia.

For some uses the grease is subjected to drastic modification. Distillation with superheated steam at 450° to 750° F. produces unsaturated hydrocarbons that appear to be dehydration products of some of the alcohols of the esters originally present. Accompanied by large volumes of hydrogen sulfide and other obnoxious gases, they distill over with some of the acids. The condensate can be separated into a liquid and a solid fraction. The liquid fraction, known as wool oleine, was formerly an important wool lubricant, but other wool oils have apparently taken its place in this country. In England it is still used in processing low-grade materials. The solid fraction, called wool stearine, and the still residue, called wool pitch, are used in high-temperature lubricants.

A relatively new development, whose application is at present probably limited to England, is the dry-saponification process, in which the grease is heated with powdered caustic soda without addition of water. The effect of the treatment is the usual conversion of the acids of the grease into sodium soaps, but the alcohol fraction is so modified that it has drying properties, that is, if spread out in a thin layer and exposed to the air it forms a tough film. The modified alcohols can be removed from the mixture by extraction with suitable solvents. Because of their drying properties they are suitable for use in protective coatings. The residual sodium soaps (and also the original saponification mixture) can be used in making lubricating greases or converted to other metallic soaps for lubricants, gland-packing materials, oil thickeners, bitumen-addition products, roofing felts, and concrete waterproofing by incorporation of the finely powdered calcium soap in cement.

SUINT IS A MIXTURE of the potassium salts of lactic, hippuric, succinic, and various fatty acids, urea, a colored substance called lanaurin, and other unidentified nitrogenous substances. Sometimes it is used in scouring, but it is seldom recovered. At various times in the past when potassium was scarce, aqueous suint solutions were evaporated and the residue calcined. In that way the organic material was eliminated and the potassium recovered as the carbonate. This expensive procedure could not compete with recovery of potassium salts from the natural deposits later found in this country.

Work done in the Department more than 25 years ago by F. P. Veitch and Leon C. Benedict showed that the dried and degreased evaporation residue from wool-scouring liquors, corresponding essentially to the suint, contained enough nitrogen and potassium and had physical properties suitable for use in fertilizers. Apparently that application has not yet been developed commercially.

FOR MEDICINAL and cosmetic purposes, wool grease is intensively purified. It is refined to remove any free fatty acids, deodorized, and bleached. The pure grades are designated as lanolin, U. S. P., or lanolin, cosmetic grade, and may be anhydrous or hydrous. As an ointment base, lanolin is superior to fats like lard in several ways. It absorbs more water and is less likely to become rancid. Because of its greater stickiness it adheres more pertinaceously to the skin; because it is difficult to saponify it is less likely to be washed off. Although wool wax penetrates the skin less readily than fats like lard, when aqueous solutions of water-soluble substances are dispersed in lanolin ointment bases they are absorbed more readily than when dispersed in lard, petrolatum, or washable ointment bases. This has been demonstrated by experiments with radioactive sodium chloride, movements of which can be readily traced in the tissues. Lanolin is used in skin-protective creams and also in the waterless ointments, in which solid medicaments are incorporated mechanically.

In cosmetics, lanolin is used with other emulsifiers in various water-in-oil and oil-in-water emulsions, such as cold creams, cleansing creams, vanishing creams, emollient creams, night creams, antiperspirants, shaving soaps, brushless shaving creams, skin lotions, lipsticks, hair oils, and shampoos. It is considered especially desirable in these applications because of its emollient qualities and its similarity to the natural oils of human skin and hair.

Sometimes wool wax is saponified and the alcohol fraction is separated and used in medical ointments and in the cosmetic preparations I mentioned. The alcohol fraction, which probably contains some residual soap and some unsaponified esters, is said to be superior to lanolin as an ointment base. This may very well be true, for the process eliminates inert constituents and impurities, which are dark and odorous, and any residual soap would probably enhance the virtues of the mixture as an emulsifying agent.

The only pure individual constituent of wool wax produced commercially is cholesterol, the raw material for the commercial preparation of vitamin D_3 and some of the sex hormones. Vitamin D_3 is one of a group of vitamins (the "sunshine" vitamins) that are useful in the prevention and treatment of rickets. A disease of infancy or early childhood, rickets is characterized by faulty ossification due to defective deposits of calcium phosphate at the growing ends of the bones. By any one of several chemical processes, cholesterol can be converted to 7-dehydrocholesterol (provitamin D_3), which becomes vitamin D_3 when it is subjected to ultraviolet radiation of a certain kind and intensity. This product is apparently identical with the natural antirachitic vitamin obtained from the fish-liver oils.

THE SEX HORMONES comprise the following: Three female-acting estrogens, estrone, estradiol, and estriol; two androgens, or male-acting hormones, testosterone and androsterone; and the gestogen, progesterone.

The estrogens act in conjunction with progesterone to control the uterine cycle. They prepare the female reproductive organs for the reception and the development of the fertilized ovum. The androgens control the development of the male genital tract and the accessory organs and they influence the longevity and mobility of the sperm. Another function of both is the induction and maintenance of the appropriate secondary sex characteristics, such as bodily contour, pitch of the voice, and distribution of hair.

In therapy, the estrogens are used in correcting functional amenorrhea, scanty menstruation, menopausal disturbances, delayed puberty, sexual frigidity, and functional sterility.

Progesterone finds application in the prevention of abortion and treatment of postpartum psychoses.

The androgens are employed in the treatment of impotence, senility, sterility, prostatism, and cryptorchidism. They also are used to alleviate the symptoms of the male climacteric corresponding to the menopause in females. They are effective in some gynecological conditions.

Testosterone is produced commercially by a series of chemical or microbiological reactions upon dehydroepiandrosterone, which is prepared from cholesterol by chromic acid oxidation of the side chain of cholesteryl acetate dibromide. Androsterone can also be derived from cholesterol, but it lost its temporary importance in hormone therapy with the discovery of the more potent testosterone. Progesterone, too, is prepared by a series of chemical reactions from cholesterol by way of the same dehydroepiandrosterone from which testosterone is derived, and some is produced from the pregnenolone isolated as a byproduct in the production of dehydroepiandrosterone from cholesterol. Estradiol, the most potent and most commonly used natural estrogen, can be prepared from cholesterol, but, like other natural hormones, it is extremely expensive. For this reason stilbestrol, the cheaper, nonsteroid synthetic estrogen, is currently more commonly used. If the natural hormones were available at a comparable price they might eventually find wider use than the synthetic substitutes.

All the foregoing uses are important, but the bulk of material so consumed is not large at present and is not likely to keep pace with the inevitable increase in production of wool grease. In the process by which cholesterol is made, byproducts are obtained that represent about 80 percent of the starting material. They consist of the acid fraction in the form of soaps, the triterpene alcohols, and the so-called wax alcohols. There is now little, if any, application for these products.

As part of a general project on the utilization of wool, there was set up in the Eastern Regional Research Laboratory in 1948 a project designed to develop processes for the utilization of the potentially valuable wool wax and suint, now largely wasted. In this project, an attempt will be made to isolate each individual constituent in a pure state and to learn as much as possible about its structure and its physical and chemical properties. Accurate knowledge of this sort will contribute to greater utilization of the original mixture as well as of the constituents themselves. It will reveal possible new uses, especially of the constituents, when the information is made available to workers in other fields.

The following are some of the problems toward which this program is directed. There is need for better methods of purifying the crude materials, methods of eliminating the sulfur, for example. The first step in isolating the constituents is saponification, the process by which the esters are broken down into their component acids and alcohols. No method at present in use is entirely satisfactory and there is much room for improvement in the methods of separating the alcohol fraction from the acids. Even more difficult is the problem of separating cholesterol in pure form and in good yield from the mixture of alcohols. An important step toward the solution of this problem will be taken when more is known about the other alcoholic constituents with which it is associated.

The structure of the triterpene alcohols has not been elucidated as yet, and their possible application as intermediates for production of hormones, chemotherapeutic agents, or other useful products depends upon more accurate knowledge of their structures.

Most of the wax alcohols remain unidentified, but they are long-chain compounds of the type useful in the preparation of surface-active agents (detergents, emulsifiers, wetting agents, penetrants, froth-flotation agents, demulsifiers), synthetic waxes, and other synthetic products, such as plasticizers.

The branched-chain fatty acids of wool wax are unique among naturally occurring fatty acids. When enough is known about them to permit development of a method of separating them, products may be derived from them which will be suitable for applications different from those of the fatty acids at present available for industrial uses.

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The work on wool grease at the Eastern Laboratory has been conducted under authority of the Research and Marketing Act of 1946. Late in 1950, the Wool Advisory Committee, set up under the Act, recommended continued emphasis on developing new industrial uses for wool grease and other wool byproducts and better methods of refining them for specific uses.